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Hydrothermal Synthesis and Structural Characterization of the High-Valent Ruthenium-Containing Polyoxoanion $[\{PW_{11}O_{39}\}_2\{(HO)Ru^{IV}–O–Ru^{IV}(OH)\}]^{10–}$

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The high-valent ruthenium-containing $[\{PW_{11}O_{39}\}_2\{(HO)Ru^{IV}–O–Ru^{IV}(OH)\}]^{10–}$ anion (**1**) has been synthesized by hydrothermal reaction and characterized by X-ray diffraction, IR, multinuclear (^{31}P and ^{183}W) NMR spectroscopy and electrochemistry. Single-crystal analysis was carried out on $Rb_{10}[\{PW_{11}O_{39}\}_2\{(HO)Ru^{IV}–O–Ru^{IV}(OH)\}]·21H_2O$, which crystallizes in the monoclinic system, space group $P2_1/n$, with a = 11.1912(14), b = 21.9257(12), c = 38.7310(96) Å, β = 94.682(19)°, V = 9472(3) Å^3, Z = 4. Polyanion **1** consists of two lacunary $[\alpha\text{-}PW_{11}O_{39}]^{7–}$ anions connected by a linear $\{(HO)Ru–O–Ru(OH)\}^{4+}$ unit. Each ruthenium ion achieves six-coordination through interaction with two terminal oxo ligands from the lacuna of each $[PW_{11}O_{39}]^{7–}$ anion.

Introduction

Lacunary polyoxometalates (POMs) are a class of inorganic ligands with a set of properties, e.g. multidenticity, rigidity, thermal and oxidative stability,[1–3] which make them quite attractive for oxidation catalysis.[4–6] In particular, the past decade has witnessed the growing interest for the incorporation of noble-metal cations into POMs.[7–14] Among the platinum metals, ruthenium has probably been the most studied,[15–28] since it offers access to the most versatile chemistry, based on a wide range of oxidation states and chemical environments. However, despite the growing number of reported Ru-containing POMs, there is a lack of suitable synthesis precursors and reliable procedures. Indeed, if different precursors were punctually used {among which $[Ru(H_2O)_6]^{2+}$, $RuCl_3·xH_2O$, $[Ru(acac)_3]$ and [*cis*-$RuCl_2(dmso)_4$]}, little effort of rationalization has been done. When searching for another entry into ruthenium POM chemistry, our group[29–35] and that of Süss-Fink[36–38] have investigated the reactivity of low-valent ruthenium organometallic precursors like $\{Ru(arene)\}^{2+}$ towards POMs. These studies have led to the description of a sizeable family of organometallic oxides and organometallic derivatives of heteropolytungstates and our approach was then extended to various POMs by several groups.[39–44] While these arene complexes extend the range of Ru-containing POMs, variable results have been obtained when looking at their reactivity.[45–47] Indeed, recent studies have shown that some $\{Ru^{II}(arene)\}^{2+}$ organometallic oxides display an interesting catalytic activity in the Dynamic Kinetic Resolution (DKR) of chiral alcohols, owing to a synergetic interaction between the Ru and M^{VI} (M = Mo, W) centers.[48] However, in most cases, particularly in the presence of oxidants, decomposition of the complexes occurs during the catalytic process.[47,49] This led us to look for other sources of ruthenium and we set our choice to the mixed-valence $[Ru_2(O_2CCH_3)_4Cl]$ complex. The present report deals with the reaction of this complex with $[\alpha\text{-}PW_{11}O_{39}]^{7–}$, which under hydrothermal conditions leads to the dimeric Ru^{IV} species $[\{PW_{11}O_{39}\}_2\{(HO)Ru^{IV}–O–Ru^{IV}(OH)\}]^{10–}$.

Results and Discussion

Synthesis and Structure

Having in mind the work of Pope who investigated the reaction of $[Rh_2(O_2CCH_3)_4]$ with $[\alpha\text{-}PW_{11}O_{39}]^{7–}$,[50] we checked the reactivity of $[Ru_2(O_2CCH_3)_4]Cl$ towards $[\alpha\text{-}PW_{11}O_{39}]^{7–}$. We did not observe any reaction in aqueous solution under conventional conditions, even not after prolonged boiling. However, a reaction occurs under hydrothermal conditions (120 °C, under autogen pressure) in water (initial pH = 2.9). The ^{31}P NMR spectrum of the resulting brown solution showed a narrow line at δ = 0.95 ppm (**A**) and a broad peak at about –63 ppm (**B**). Upon acidification from pH = 3.8 (natural pH after reaction) to 1, the position of **A** was not changed while that of **B** shifted from –63 to –83 ppm (see Figure S1 in the Supporting Information). The latter was unambiguously as-

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signed to the paramagnetic $[Ru^{III}(H_2O)PW_{11}O_{39}]^{4-}$ anion, by comparison with the ^{31}P NMR chemical shift.[15]

Addition of an excess of RbCl led to the formation of a gold-brown precipitate in which the new Ru^{IV} derivative $Rb_{9.5}K_{0.5}[\{PW_{11}O_{39}\}_2\{(HO)Ru^{IV}–O–Ru^{IV}(OH)\}]\cdot 18H_2O$ (**$Rb_{9.5}K_{0.5}$-1**) appeared to be the major species according to ^{31}P NMR (δ = 0.6 ppm). After recrystallization from boiling water, the yield in **$Rb_{9.5}K_{0.5}$-1** was 16%, based on Ru. Crystals of **$Rb_{9.5}K_{0.5}$-1** proved to be unsuitable for X-ray crystallography. A further crop of crystals was obtained once by slow evaporation of the filtrate after separation of the gold-brown precipitate resulting from the addition of RbCl. Although these crystals were found to decompose very quickly outside the mother solution, an X-ray crystal structure determination could be achieved, which led to the formula $Rb_{10}[\{PW_{11}O_{39}\}_2\{(HO)Ru^{IV}–O–Ru^{IV}(OH)\}]\cdot 21H_2O$ (**Rb_{10}-1**$\cdot 21H_2O$).

Rb_{10}-1$\cdot 21H_2O$ crystallizes in the monoclinic $P2_1/n$ space group. The asymmetric unit contains one anion, 10 rubidium cations and 21 molecules of water, all in general positions. The anion **1** (Figure 1) consists of two lacunary $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ anions connected by an almost linear $\{(HO)Ru^{IV}–O–Ru^{IV}(OH)\}$ unit [Ru–O–Ru angle: 175.2(11)°, O–Ru–O angles: 178.5(7)° and 178.0(8)°]. Each Ru^{IV} ion achieves six-coordination through interaction with two terminal oxo ligands from the lacuna of each $[PW_{11}O_{39}]^{7-}$ anion, these four oxygen atoms providing a square planar environment. Although the anion has no crystallographically-imposed symmetry, it displays approximate C_{2v} symmetry with the pseudo-C_2 axis passing through the central oxo ligand and being perpendicular to the Ru–O–Ru axis. The four tungsten atoms adjacent to Ru are not equivalent, and, consequently, the Ru–O–W angles are also different. Two angles are nearly linear (average value 171.01°) while the two other ones are more acute (average value 153.02°). The distances between the Ru ion and the oxygen atoms of the $\{PW_{11}\}$ units are in the range 1.965(15)–2.014(14) Å. The geometrical features of the bridging Ru–O–Ru unit [$d(Ru–O_b)$ = 1.765(11) and 1.784(11) Å] are consistent with those expected for a $Ru^{IV}–O–Ru^{IV}$ moiety from the literature, like in $[Cl_5Ru^{IV}–O–Ru^{IV}Cl_5]^{4-}$ (1.798 Å).[51] They are also in agreement with the diamagnetism of the compound. The Ru–OH bond lengths [2.016(14) and 2.028(14) Å] are in accordance with the literature for Ru^{IV}–OH-containing compounds.[52–57] Indeed the $\{Ru^{IV}–H_2O\}$ bond lengths usually lie in the range 2.1 to 2.2 Å,[54,58–60] although they are shorter [2.042(4) Å] in $[Cl_4(H_2O)Ru^{IV}–N–Ru^{IV}(H_2O)Cl_4]^{3-}$.[53] BVS calculations[61] on Ru also support this description. Indeed, the calculated valences are +4.39 and +4.47, respectively, for both Ru ions.[62–65] Furthermore, the description of the bridging unit is in complete agreement with the spectroscopic data (vide infra). The geometry of the $\{PW_{11}\}$ units is only slightly altered with respect to the "free" (in fact sodium complex) $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ anion.[66]

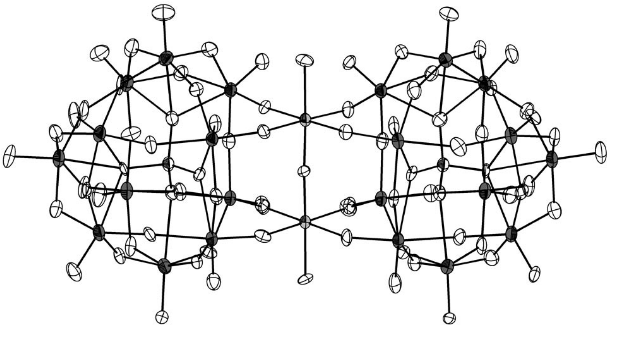

Figure 1. Structural representation of the anion **1**. Thermal ellipsoids of oxygen (white), phosphorus (white with quadrants), tungsten (medium grey) and ruthenium atoms (light grey) are shown at the 30% level.

The overall features of **1** are quite similar to those of the anion $[\{\alpha_2\text{-}P_2W_{17}O_{61}\}_2\{(Cl)Ru^{IV}–O–Ru^{IV}(Cl)\}]^{16-}$ obtained by Finke through reaction of $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ with $RuCl_3\cdot H_2O$.[16] The latter has been obtained by recrystallization in an LiCl aqueous solution of the hydroxo parent $[\{\alpha_2\text{-}P_2W_{17}O_{61}\}_2\{(HO)Ru^{IV}–O–Ru^{IV}(OH)\}]^{16-}$, for which no structure is available.

Both complexes differ markedly from the dimeric $[\{SiW_{11}O_{39}\}_2\{Ru^{IV}–O–Ru^{IV}\}]^{10-}$ described by Sadakane:[24,67,68] i) in our case, the ruthenium ions are not integrated but "supported" on the POM framework and each of them is linked to both $\{PW_{11}\}$ unit; ii) the Ru–O–Ru bridge is bent in Sadakane's complex [Ru–O–Ru angle: 154.4(7)°]; iii) then there is no extra ligand in Sadakane's complex, since each $\{SiW_{11}\}$ unit acts as a pentadentate ligand, with coordination of an oxygen atom from the central SiO_4.

More generally, this complex is the second example of a Ru^{IV} derivative of the $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ anion. We thus have shown that it has been possible to obtain a new complex, which is different from the $[PW_{11}O_{39}\{Ru^{IV}=O\}]^{5-}$ described by Pope and co-workers,[15] by varying at once the ruthenium precursors and the reaction conditions. To the best of our knowledge, it is the first time that the dimeric $[Ru_2(O_2CCH_3)_4]^+$ complex is successfully used for the synthesis of ruthenium derivatives of POMs.

^{31}P and ^{183}W NMR Spectroscopy

Magnetic susceptibility measurements (on SQUID) show that the title complex is diamagnetic. This is in agreement with the narrow ^{31}P NMR signal of this compound in contrast to paramagnetic ruthenium-containing tungstophosphates.[15] Indeed, as described above, the chemical shift of the rubidium salt of anion **1** is 0.6 ppm in pure water, with half-width ($\Delta\nu_{1/2}$ = 12 Hz) (see Figure S2 in the Supporting Information). This chemical shift is, however, unusual for diamagnetic ruthenium-, and more generally for diamagnetic metallic-containing derivatives of the $[PW_{11}O_{39}]^{7-}$ anion. Nevertheless, it is noteworthy that a similar value(δ = +0.2 ppm) was observed for the signal arising from the phosphorus atoms closer to the Ru–O–Ru bridge in the related $[\{\alpha_2\text{-}P_2W_{17}O_{61}\}_2\{(HO)Ru^{IV}–O–Ru^{IV}(OH)\}]^{16-}$ anion.[16]

The ^{183}W NMR spectrum of the Li^+ salt of **1** recorded at 333 K for solubility reasons (Figure 2) displays six major

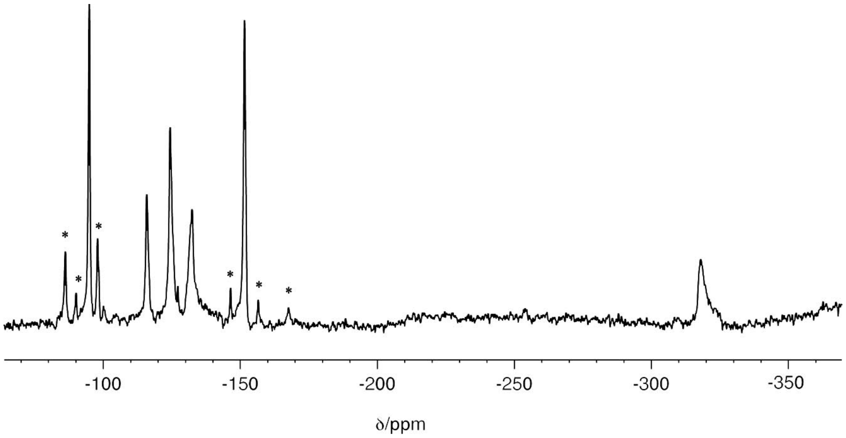

Figure 2. (20.8 MHz) ^{183}W NMR spectrum of the Li^+ salt of **1**. The peaks topped by the symbol * are due to impurities (see Discussion).

lines along with minor lines which chemical shifts correspond to the $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ anion. The latter arises from partial decomposition of **1** upon cation exchange as shown by ^{31}P NMR spectroscopy. The six-line pattern of **1** (with approximate 2:1:2:2:2:2 relative intensities) is consistent with the pseudo-C_{2v} symmetry observed in the solid state. Four of these six lines are relatively narrow ($\Delta\nu_{1/2}$ in the range 9–19 Hz) and in the usual range of chemical shift for diamagnetic species (–90 to –155 ppm). However, the two other lines, at –132.4 and –317.8 ppm, are significantly broader ($\Delta\nu_{1/2}$ = 40 and 50 Hz, respectively) and are tentatively assigned to the W atoms close to the Ru centres. It is worth noting that one of these two lines is strongly shifted to low frequency (–317.8 ppm). This is another similar feature to $[\{\alpha_2\text{-}P_2W_{17}O_{61}\}_2\{(HO)Ru^{IV}\text{–}O\text{–}Ru^{IV}(OH)\}]^{16-}$ where one of the tungsten resonances is also strongly shifted (δ = –305 ppm). Other diamagnetic ruthenium derivatives of the $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ anion have been characterized. The $[PW_{11}O_{39}\{Ru^{II}(L)\}]^{5-}$ anions (L = H_2O, DMSO), which have been first isolated by Rong and Pope,[15] and the recently described $[PW_{11}O_{39}\{Ru^{VI}N\}]^{4-}$ nitrido derivative[69] all present a six-line pattern according to their C_s symmetry. In all cases, the signals of the W atoms remote from the ruthenium fall in the range –80 to –150 ppm, while the chemical shifts of the adjacent W atoms depend on the oxidation state of Ru. These W nuclei have chemical shifts equal to –134.4 and –91.0 ppm in $[PW_{11}O_{39}\{Ru^{VI}N\}]^{4-}$, while they are strongly deshielded in both Ru^{II} derivatives (L = H_2O, δ = +292.8 and +159.3 ppm, L = DMSO, δ = +117.4 and –2.7 ppm).[15,21,32] Nevertheless it is difficult to compare these complexes since i) the number of d electrons of the ruthenium is different in all these complexes, and ii) in the title compound, Ru–O–W angles are higher than in the $[PW_{11}O_{39}\{RuL\}]^{n-}$ species, due to the specific linking of the Ru atoms in **1**.

Spectroscopic and Electrochemical Characterization of Anion 1

The UV/Vis spectrum of the compound (Figure S3) displays a band centered at 418 nm (ε = 1.48 10^4 mol^{-1} dm^3 cm^{-1}), close to that observed for the $[\{\alpha_2\text{-}P_2W_{17}O_{61}\}_2\{(Cl)Ru^{IV}\text{–}O\text{–}Ru^{IV}(Cl)\}]^{16-}$ anion.[16] The attribution of this transition is not straightforward since, to the best of our knowledge, no molecular orbital calculations have been done on compounds that contain such a $[(HO)Ru^{IV}\text{–}O\text{–}Ru^{IV}(OH)]^{4+}$ unit. Indeed, even if the electronic spectrum of the dimeric $[Cl_5Ru^{IV}\text{–}O\text{–}Ru^{IV}Cl_5]^{4-}$ has been known for decades, it has been only recently demonstrated that its band at 490 nm arises from a $\pi^*_{Ru\text{–}O\text{–}Ru}\leftarrow\pi_{Ru\text{–}Cl}$ transition.[70] Nevertheless, these data also confirm the oxidation state +IV in **1**, since $\{Ru^{III}\text{–}O\text{–}Ru^{III}\}$ bridges are usually characterized by a band at lower energy (in the range 580–670 nm) assigned to a $Ru\leftarrow O^{2-}$ charge transfer transition.[71,72]

The Raman spectrum of compound **$Rb_{9.5}K_{0.5}$-1** has been recorded in the solid state and compared to $K_7[PW_{11}O_{39}]\cdot 14H_2O$, $Cs_5[PW_{11}O_{39}\{Ru(p\text{-cymene})(H_2O)\}]\cdot xH_2O$,[32] and commercial $K_4[Cl_5Ru^{IV}\text{–}O\text{–}Ru^{IV}Cl_5]$ (Figure 3). Indeed it has been previously shown that the position of the Raman-active $\nu(Ru\text{–}O\text{–}Ru)_{sym}$ band is characteristic of the oxidation state of the metals in the bridge. For example, alkaline salts of $[Cl_5Ru^{IV}\text{–}O\text{–}Ru^{IV}Cl_5]^{4-}$ display a very strong band in the range 249–256 cm^{-1}.[73] For Ru^{III} derivatives, the $\nu(Ru\text{–}O\text{–}Ru)_{sym}$ depends strongly upon the M–O–M angle but should lie in the region 300–500 cm^{-1} depending on the angle.[54] This band is systematically accompanied by a broad and weaker one, which has been attributed to its first overtone $2\nu_{sym}$ at twice the energy.[74,75] The Raman spectrum of compound **1** displays a relatively intense and narrow band at 289 cm^{-1}, which does not appear in the spectra of $K_7[PW_{11}O_{39}]\cdot 14H_2O$ and $Cs_5[PW_{11}O_{39}\{Ru(p\text{-cymene})(H_2O)\}]\cdot xH_2O$. Furthermore, no band is observed at about 580 cm^{-1} that could correspond to $2\nu_{sym}$. It also displays a band at 369 cm^{-1}, but a similar feature can be observed in the spectrum of $Cs_5[PW_{11}O_{39}\{Ru(p\text{-cymene})(H_2O)\}]\cdot xH_2O$, and we assigned it to a W–O–Ru vibration band. For these reasons, and because of its position at low energy, the band at 289 cm^{-1} can reasonably be attributed to $\nu(Ru^{IV}\text{–}O\text{–}Ru^{IV})_{sym}$. The IR spectrum of **$Rb_{9.5}K_{0.5}$-1** (Figure S4) displays strong bands in the region 950 to 700 cm^{-1} classically attributed to $\nu_{W=Ot}$ (949 cm^{-1}) and $\nu_{W\text{–}O\text{–}W}$ (898, 848, 787 cm^{-1}). The IR-active ν(Ru^{IV}–O–Ru^{IV})$_{asym}$ band is expected in this region,[73] but is impossible to be distinguished from the $\nu_{W=Ot}$ and ν_{W-O-W} bands, if not too weak to be observed. In addition this spectrum shows two well-separated bands at higher energy (1089 and 1038 cm^{-1}) attributed to the {P=O} vibrators. The splitting of the ν_{P-O} stretching mode is comparable to the one observed in the free lacunary [α-$PW_{11}O_{39}$]$^{7-}$ anion (Δν ≈ 45 cm^{-1}), in agreement with the absence of interaction of Ru addenda atoms with the oxygen atoms of the {PO_4} group.

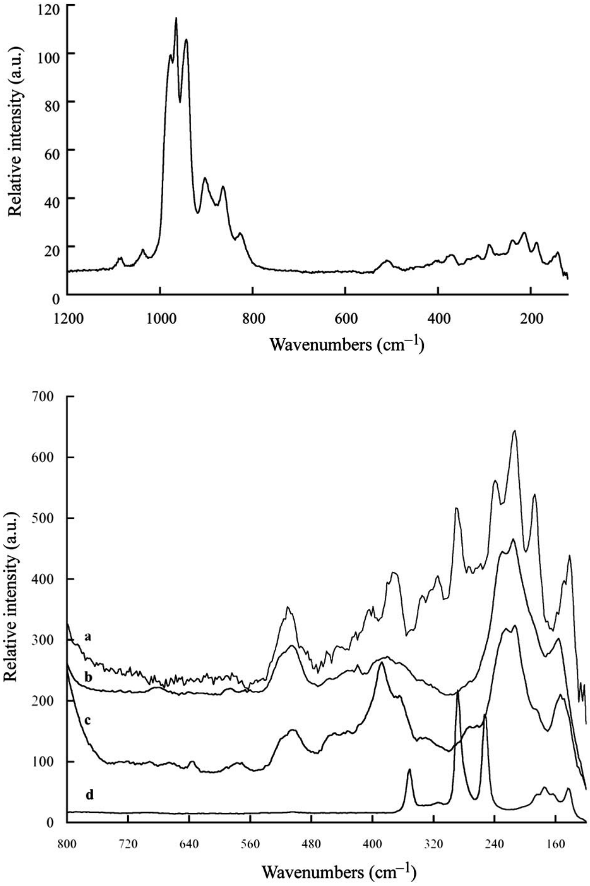

Figure 3. Raman spectrum of **$Rb_{9.5}K_{0.5}$-1** in the range 120–1200 cm^{-1} (Figure 3, top); comparison of the Raman spectra of **$Rb_{9.5}K_{0.5}$-1** (a), $K_7[PW_{11}O_{39}]\cdot 14H_2O$ (b), $Cs_5[PW_{11}O_{39}$-{Ru(*p*-cymene)(H_2O)}]·*x*H_2O (c) and $K_4[Cl_5Ru^{IV}–O–Ru^{IV}Cl_5]$ (d) in the range 120–800 cm^{-1} (Figure 3, bottom). The spectra have been shifted for clarity.

Cyclic voltammetry of **$Rb_{9.5}K_{0.5}$-1** at pH = 3 in a sulfate buffer reveals the presence of a reduction wave at $E_{1/2}$ = –0.02 V and an oxidation wave at +0.65 V vs. SCE (Figure 4). Polarography of this system confirms that the intensity of the reduction wave is twice than that of the oxidation one (see supporting information Figure S5). Both waves are reversible at a stationary carbon electrode. We can then assume that the first couple at –0.02 V is very probably a two electrons transfer and can be assigned to the $Ru^{IV}{}_2/Ru^{III}{}_2$ process while the second couple at +0.65 V should be a single-electron transfer and therefore assigned to the $Ru^VRu^{IV}/Ru^{IV}{}_2$ couple. We were not able to observe the oxidation of the second Ru^{IV} into Ru^V. Both processes were found to be pH-independent in the pH range from 1–4, and it was not possible to observe the splitting of the reduction wave by varying pH.

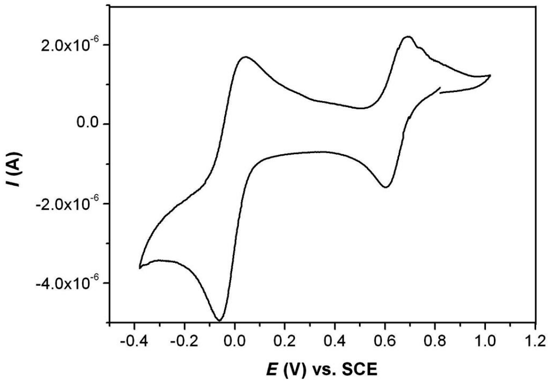

Figure 4. Cyclic voltammogram of compound **$Rb_{9.5}K_{0.5}$-1** (pH = 3).

Summary and Conclusion

In this paper we have described the synthesis of a new water-soluble Ru^{IV}-containing heteropolytungstate, namely [{$PW_{11}O_{39}$}$_2$\{(HO)Ru^{IV}–O–Ru^{IV}(OH)\}]$^{10-}$, that has been obtained by reaction of [α-$PW_{11}O_{39}$]$^{7-}$ with [$Ru_2(CH_3CO_2)_4Cl$] under hydrothermal conditions and isolated as a rubidium salt. It has been characterized in solution by ^{31}P and ^{183}W NMR spectroscopy and by electrochemistry, and in the solid state by Raman and IR spectroscopy. Single-crystal structural analysis of Rb_{10}[{$PW_{11}O_{39}$}$_2$\{(HO)Ru^{IV}–O–Ru^{IV}(OH)\}]·21H_2O revealed that the anion consists of two [α-$PW_{11}O_{39}$]$^{7-}$ anions connected by a quasi-linear \{(HO)-Ru^{IV}–O–Ru^{IV}(OH)\}$^{4+}$ bridging unit. It is only the third Ru^{IV}-containing POM to be structurally characterized. Previous examples were [(α_2-$P_2W_{17}O_{61}$)$_2$(XRu^{IV}–O–Ru^{IV}X)]$^{16-}$ (X = Cl and OH)[16] and [(α-$SiW_{11}O_{39}$)$_2$(Ru^{IV}–O–Ru^{IV})]$^{10-}$.[68] The ability of POMs to stabilize high-valent oxometal units is well established[8,9,13,76] and the analogy of the resulting complexes to metalloporphyrins or corroles, as well as to the active site of cytochrome P-450, has been theoretically addressed.[77] Expansion of the chemistry of high-valent oxo-ruthenium POMs is still dependent on the development of appropriate synthesis routes. Our current efforts are focused on this point.

Experimental Section

Materials and Methods: Reagents and solvents were obtained from commercial sources and used as received. The precursors $K_7[PW_{11}O_{39}]\cdot 14H_2O$[78] and [$Ru_2(O_2CCH_3)_4Cl$][71] were prepared as described in the literature. IR spectra were recorded from KBr pellets on a Biorad FT 165 spectrometer. Raman spectra were collected with a Kaiser Optical Systems HL5R Raman spectrometer equipped with a near-IR laser diode working at 785 nm. The ^{31}P NMR solution spectra were recorded at 121.5 MHz, in 5 mm o.d. tubes on a Bruker Avance 300 spectrometer equipped with a QNP probehead. The ^{183}W NMR spectrum was recorded in 10 mm o.d. tubes at 20.8 MHz on a Bruker DRX500 spectrometer equipped with a broadband VSP probehead. Chemical shifts are referenced with respect to external 85% H_3PO_4 (^{31}P) and to external alkaline 2 M Na_2WO_4 aqueous solution (^{183}W), respectively, and were measured by the substitution method. For ^{183}W a saturated aqueous solution of $H_4SiW_{12}O_{40}$ was used as secondary standard (δ = –103.8 ppm).

The ^{183}W NMR spectrum of $[\{PW_{11}O_{39}\}_2\{(HO)Ru^{IV}–O–Ru^{IV}(OH)\}]^{10-}$ (**1**) was recorded on a concentrated aqueous solution of the lithium salt obtained by cation exchange (Dowex 50, lithium form). The electronic absorption spectrum was recorded with a Shimadzu UV-2101 PC spectrometer. Elemental analyses were performed by the Service Central d'Analyse of the CNRS (Vernaison, France). Electrochemical data were obtained in a 0.2 M Na_2SO_4/H_2SO_4 buffer (pH = 3.0) with a concentration of **$Rb_{9.5}K_{0.5}$-1** equal to 0.5×10^{-3} mol L^{-1}. Cyclic voltammetry at a carbon electrode was carried out using the EG&G model 273A system. A standard three-electrode cell was used, which consisted of the working electrode, an auxiliary platinum electrode, and an aqueous saturated calomel electrode (SCE) equipped with a double junction. The scan rate was of 20 mV/s. Polarography was carried out using a Radiometer POL 150 polarographic stand with a rotating carbon electrode. Potentials are relative to SCE. The magnetic susceptibility of **$Rb_{9.5}K_{0.5}$-1** was recorded in the temperature range between 2 K and 300 K on a Quantum Design MPMS Superconducting Quantum Interference Device SQUID magnetometer. Combined thermogravimetric and differential thermal analyses were performed under N_2 flow (100 mL/min) at a heating rate of 3 °C/min in a Pt crucible on a SEIKO TG-DTA 320 thermal analyser operated by a SEIKO SSC5200 disk station. The sample mass was about 34 mg.

Synthesis of $Rb_{9.5}K_{0.5}[\{PW_{11}O_{39}\}_2\{(HO)Ru^{IV}–O–Ru^{IV}(OH)\}]\cdot 18H_2O$ ($Rb_{9.5}K_{0.5}$-1): A 0.5 g (0.156 mmol) sample of $K_7[PW_{11}O_{39}]\cdot 14H_2O$ was dissolved in 6 mL of water. The pH of the solution was adjusted to 2.9 by addition of 1 M HCl, and $[Ru_2(O_2CCH_3)_4]Cl$ (0.0352 g, 0.074 mmol) was added. The mixture was placed in a Teflon-lined Parr acid digestion bomb at 120 °C for 24 h and then cooled to room temperature. RbCl (0.29 g, 2.4 mmol) was added, leading to the precipitation of a brown solid (yield 0.18 g), which was separated by filtration, washed successively with 10 mL of methanol and diethyl ether, and then air-dried. The solid was recrystallized from the minimum amount of boiling water; dark red crystals settled within one day; they were filtered off and washed with methanol and diethyl ether and analyzed; the formula $Rb_{9.5}K_{0.5}[\{PW_{11}O_{39}\}_2\{(HO)Ru^{IV}–O–Ru^{IV}(OH)\}]\cdot 18H_2O$ (**$Rb_{9.5}K_{0.5}$-1**) was assigned on the basis of elemental and thermogravimetric analyses (yield 0.076 g, 16%, based on Ru). IR (KBr): $\tilde{\nu}$ = 1089, 1038, 949, 898, 848, 787 cm^{-1}. ^{31}P NMR (H_2O/D_2O, 1:1): δ = 0.6 (s) ppm. ^{183}W NMR (Li^+ salt aqueous solution): δ = –94.9 (2 W), –115.9 (1 W), –124.4 (2 W), –132.4 (2 W), –151.5 (2 W), –317.8 (2 W) ppm. UV/Vis (H_2O): λ_{max} (ε) = 418 nm (1.48×10^4 mol^{-1} dm^3 cm^{-1}). $H_2K_{0.5}O_{81}P_2Rb_{9.5}Ru_2W_{22}\cdot 18H_2O$ (6762.30): calcd. Rb 12.01, K 0.29, Ru 2.99, P 0.92, W 59.81, H_2O 4.79; found Rb 11.11, K 0.27, Ru 2.68, P 0.95, W 58.20, H_2O 4.80.

X-Ray Diffraction Study: Crystal data for **Rb_{10}-1**$\cdot 21H_2O$. Dark red crystals; monoclinic, $P2_1/n$, a = 11.1912(14), b = 21.9257(12), c = 38.7310(96) Å, β = 94.682(19)°, V = 9472(3) Å^3, Z = 4, T = 293(2) K, μ = 32.163 mm^{-1}, 94636 reflections measured, 26906 independent (R_{int} = 0.0810), 13671 observed [$I = 2\sigma(I)$], 1147 parameters, final R indices R_1 = 0.0766 [$I = 2\sigma(I)$] and wR_2 = 0.1492 (all data), GOF on F^2 = 0.992, max./min. residual electron density: 5.18/–3.87 e Å^{-3}. A single crystal of compound **Rb_{10}-1**$\cdot 21H_2O$ was selected and introduced into a Lindemann tube with two drops of the mother liquor on each side of the crystal in order to avoid loss of lattice water. Intensity data were collected with a Bruker-Nonius Kappa-CCD diffractometer with graphite-monochromated Mo-K_α radiation. Unit-cell parameters determination, data collection strategy and integration were carried out with the Nonius EVAL-14 suite of programs.[79] The structure was solved by direct methods using the SHELXS-97 program[80] and refined anisotropically by full-matrix least-squares methods using the SHELXL-97 software package.[80]

The crystallographic CIF file for **Rb_{10}-1** has been deposited at Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany. Data can be obtained on quoting the depository number CSD-418642.

Supporting Information (see also the footnote on the first page of this article): ^{31}P NMR spectrum, IR spectrum, UV/Vis spectrum and polarogram in 0.2 M Na_2SO_4/H_2SO_4 buffer (pH = 3.0) of compound **$Rb_{9.5}K_{0.5}$-1**. ^{31}P NMR spectra of the mother liquor in the synthesis of **1** as a function of the pH.

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